## **Supplementary Information**

# A Hierarchical Hollow Pt@H-UiO-66-NH<sub>2</sub>/CdS Ternary Catalyst for Efficient Visible Light Prompted Photocatalysis

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#### 1. Synthesis of contrast catalysts

#### **1.1 Synthesis of Pt NPs**

The Pt NPs were synthesized according to the reported method with some modifications.<sup>S1</sup> Typically, 222 mg poly(vinylpyrrolidone) (PVP, MW = 55,000) was dissolved in 20 mL of ethylene glycol in a round-bottomed flask. Then 50.75 mg H<sub>2</sub>PtCl<sub>6</sub>·6H<sub>2</sub>O was added and dissolved thoroughly. The solution was heated to 180 °C and maintained at this temperature for 10 min, then the as-synthesized Pt NPs were precipitated by acetone and collected by centrifugation at 9,000 rpm for 5 minutes. The sample was washed with n-hexane for three times to remove excess free PVP and was finally dissolved in 16 mL of deionized water for further use.

#### 1.2 Synthesis of H-UiO-66-NH<sub>2</sub>/CdS and UiO-66-NH<sub>2</sub>/CdS

For comparison purposes, H-UiO-66-NH<sub>2</sub>/CdS was synthesized in the same way as Pt@H-UiO-66-NH<sub>2</sub>/CdS except that Pt@H-UiO-66-NH<sub>2</sub> was replaced by H-UiO-66-NH<sub>2</sub>. UiO-66-NH<sub>2</sub>/CdS was synthesized in the same way as Pt@H-UiO-66-NH<sub>2</sub>/CdS except that Pt@H-UiO-66-NH<sub>2</sub> was replaced by UiO-66-NH<sub>2</sub>.

### 2. Figures and tables



**Fig. S1** SEM micrographs of (a) H-UiO-66-NH<sub>2</sub>, (b) Pt@H-UiO-66-NH<sub>2</sub>, (c) H-UiO-66-NH<sub>2</sub>/CdS, (d) UiO-66-NH<sub>2</sub>/CdS, (e) Pt@UiO-66-NH<sub>2</sub>/CdS and (f) Pt@H-UiO-66-NH<sub>2</sub>/CdS.



Fig. S2 Powder XRD patterns of UiO-66-NH<sub>2</sub>, UiO-66-NH<sub>2</sub>/CdS, Pt@UiO-66-NH<sub>2</sub> and Pt@H- UiO-66-NH<sub>2</sub>/CdS.



**Fig. S3** (a) UV–vis absorption spectra of Pt@UiO-66-NH<sub>2</sub>/CdS, Pt@UiO-66-NH<sub>2</sub>, UiO-66-NH<sub>2</sub>/ CdS and CdS; (b) photoluminescence spectra, (c) transient photocurrent response and (d) EIS Nyquist plots at light of Pt@UiO-66-NH<sub>2</sub>/CdS, Pt@UiO-66-NH<sub>2</sub> and UiO-66-NH<sub>2</sub>/CdS.



**Fig. S4** (a) XPS survey spectrum H-UiO-66-NH<sub>2</sub>, H-UiO-66-NH<sub>2</sub>/CdS, Pt@H-UiO-66-NH<sub>2</sub> and Pt@H-UiO-66-NH<sub>2</sub>/CdS; high resolution XPS survey spectrum of (b) Cd 3d.



Fig. S5 five continuous cycles of photocatalytic  $H_2$  production of Pt@H-UiO-66-NH<sub>2</sub> /CdS.

Five cycles had been done, showing as the Fig. S5. In some systems, a certain amount of sacrificial agent is added during each cycle to ensure the photostability. But our system is a closed test environment. We didn't add extra sacrificial agent after each cycle, so there is somewhat decline of the hydrogen evolution after the third cycle.



**Fig. S6** Curves of Kubelka-Munk function as the vertical axis and plotted against the photon energy.

entry	catalyst	BET surface area (m <sup>2</sup> /g)
1	UiO-66-NH <sub>2</sub>	619
2	H-UiO-66-NH <sub>2</sub>	471
3	Pt@H-UiO-66-NH <sub>2</sub> /CdS	351

Table S1 BET surface area of the materials.

**Table S2** Photocatalytic degradation rate constant of MB over the varied MOF-basecatalysts.

Catalyst	1	2	3	Average Value
Pt@H-UiO-66-NH <sub>2</sub>	2.28	2.07	2.02	2.12
UiO-66-NH <sub>2</sub> /CdS	4.72	4.17	3.93	4.27
H-UiO-66-NH <sub>2</sub> /CdS	5.51	5.49	4.94	5.31
Pt@UiO-66-NH <sub>2</sub> /CdS	6.68	6.11	6.08	6.29
Pt@H-UiO-66-NH <sub>2</sub> /CdS	10.89	10.25	8.5	9.88

Table S2 have listed the *Rate Constant*  $\times$  10<sup>-3</sup> and the corresponding *Average value* from three experiments for the varied MOF-base catalysts.

Photocatalyst	Light	Sacrificial agent	$H_2$ production rate (µmol h <sup>-1</sup> g <sup>-1</sup> )	Ref.
Pt@H-UiO-66-NH <sub>2</sub> /CdS	Visible light	$Na_2S/Na_2SO_3$	12810	This work
Cd <sub>0.2</sub> Zn <sub>0.8</sub> S@UiO-66-NH <sub>2</sub>	> 420 nm	$Na_2S/Na_2SO_3$	5846	S2
CdS/UiO-66	> 380 nm	Lactic acid	1725	S3
Pt@MIL-125/Au	> 380 nm	TEOA	1743	S4
MoS <sub>2</sub> @Cd-MOF	Visible light	$Na_2S/Na_2SO_3$	5587	S5
CdS@UiO-66@Pt	> 420 nm	TEOA	660.5	S6
Au@NH <sub>2</sub> -UiO-66/CdS	> 420 nm	Lactic acid	664.9	S7
NH <sub>2</sub> -UiO-66/CdS	> 420 nm	Lactic acid acetonitrile	16500	S8
BW/UiO-66/CdS	Visible light	Lactic acid	10185	S9

**Table S3** Comparison of the other MOF-based photocatalysts reported in literatures.

#### **Reference:**

[S1] T. Teranishi, M. Hosoe, T. Tanaka and M. Miyake, J. Phys. Chem. B, 1999, 103, 3818.

[S2] Y. Su, Z. Zhang, H. Liu and Y. Wang, Appl. Catal. B: Environ., 2017, 200, 448.

[S3] H.Q. Xu, S. Yang, X. Ma, J. Huang and H.L. Jiang, ACS Catal., 2018, 8, 11615.

[S4] J.D. Xiao, L. Han, J. Luo, S.H. Yu and H.L. Jiang, Angew. Chem. Int. Ed., 2018, 57, 1103.

[S5] L. Lin, S. Huang, Y. Zhu, B. Du, Z. Zhang, C. Chen, X. Wang and N. Zhang, *Dalton Trans.*, 2019, **48**, 2715.

[S6] S. Peng, Y. Jiang, Z. Wang, X, Luo, J. Lu, L. Han and Y. Ding, *Catal. Lett.*, 2020, **150**, 3533.

[S7] Z. Li, J. Zi, X. Luan, Y. Zhong, M. Qu, Y. Wang and Z. Lian, Adv. Funct. Mater., 2023, 33, 2303069.

[S8] Z. Lian, Z. Li, F. Wu, Y. Zhong, Y. Liu, W. Wang, J. Zi and W. Yang, *Commun. Chem.*, 2022, **5**, 93.

[S9] H. Fang, Z. Zhuang and D. Liu, *Langmuir*, 2022, **38**, 11590.